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Guanidinate borohydride derivatives of lanthanides: synthesis and molecular structures of the $[(Me_3Si)_2NC(NCy)_2]Gd(BH_4)_2DME$ and $[\{(Me_3Si)_2NC(NPr^i)_2\}_2Sm(BH_4)_2]^-[Li(DME)_3]^+$ complexes. Catalytic activity of the $[(Me_3Si)_2NC(NCy)_2]_2Ln(BH_4)_2Li(THF)_2$ complexes (Ln = Nd, Sm, or Yb) in methyl methacrylate polymerization*

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The reaction of $Gd(BH_4)_3(THF)_2$ with two equivalents of sodium *N*,*N*′-dicyclohexyl-*N*″-bis(trimethylsilyl)guanidinate in THF followed by the treatment of the reaction product with 1,2-dimethoxyethane produced the monoguanidinate bis(borohydride) complex $[(Me_3Si)_2NC(NCy)_2]Gd(BH_4)_2DME$ (**1**) (Cy is cyclohexyl). The treatment of the heterobimetallic samarium complex $\{(Me_3Si)_2NC(NPr^i)_2\}_2Sm(BH_4)_2Li(THF)_2$, in which the lanthanide and lithium atoms are linked by two bridging borohydride groups, with 1,2-dimethoxyethane afforded the ionic complex $[\{(Me_3Si)_2NC(NPr^i)_2\}_2Sm(BH_4)_2]^-[Li(DME)_3]^+$ (**2**). The structures of complexes **1** and **2** were established by X-ray diffraction. The $[(Me_3Si)_2NC(NCy)_2]_2Ln(BH_4)_2Li(THF)_2$ complexes (Ln = Nd (**3**), Sm (**4**), or Yb (**5**)) were found to catalyze methyl methacrylate polymerization.

Key words: lanthanides, guanidinate ligand, *N*,*N*-ligand, borohydride ligand, synthesis, structure.

Chelate guanidinate ligands have found wide application in coordination and organometallic chemistry as stabilizing groups and were used in the synthesis of a wide range of *d*-transition and main-group metal derivatives.[1] Recently, guanidinate ligands have been successfully used in the chemistry of rare earth metals for the synthesis of highly reactive alkyl and hydride derivatives.[2—9] Lanthanide borohydride complexes are of great interest because of their structural diversity[10] and high catalytic activity in polymerization of lactones,[11,12] methyl methacrylate,[13] and isoprene.[14] Recently, we have synthesized and characterized a series of lanthanide bis(guanidinate) borohydride complexes. The use of these complexes as initiators for the polymerization of lactides allows the reactions to be performed at high rate at room temperature under controlled conditions resulting in the formation of high-molecular-weight polymers with very low polydispersity (1.09).[15]

Metallocene-type borohydride complexes are generally synthesized by the reactions of the corresponding chloride derivatives with $NaBH_4$ or $LiBH_4$ in tetrahydrofuran or diethyl ether.[10] A convenient procedure for the synthesis of both bis(borohydride) and monoborohydride complexes is based on the reactions of lanthanide tris(borohydrides) $Ln(BH_4)_3(THF)_n$ with alkali metal salts LM (M = Na or K) of the corresponding ligands.[11,14,16,17] The reactions are completed in 8 h and produce the borohydride complexes in high yields. As a rule, the alkali metal borohydrides MBH_4, which are also formed in the reactions, do not complicate the isolation of the target products.

Recently,[18] we have found that the reactions of the bis(guanidinate) chloride derivatives $[\{(Me_3Si)_2NC(NPr^i)_2\}_2LnCl]_2$ (Ln = Nd or Sm) with $NaBH_4$ are more complex than those of the cyclopentadienyl derivatives. In some cases, the redistribution of the ligands was observed, producing monoguanidinate bis(borohydride) derivatives instead of the expected bis(guanidinate) borohydride complexes regardless of the ratio of the starting reagents.

In the present study, we synthesized new guanidinate borohydride derivatives of lanthanides and investigated the catalytic activity of the $[(Me_3Si)_2NC(NCy)_2]_2Ln(BH_4)_2Li(THF)_2$ complexes

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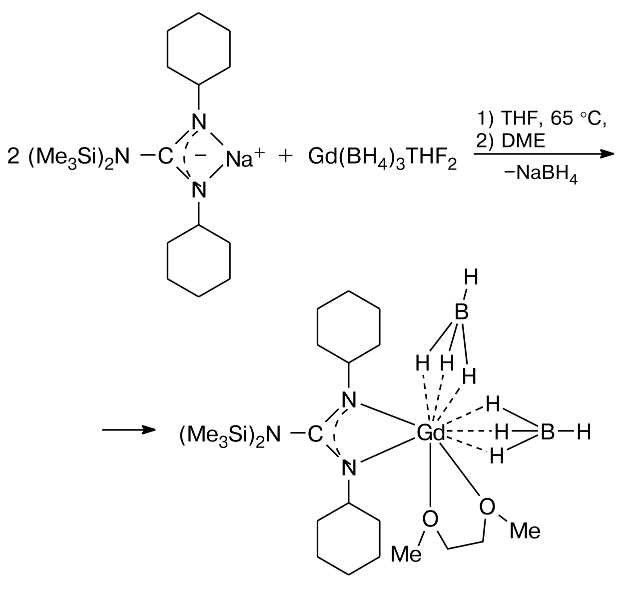
(Ln = Nd, Sm, or Yb; Cy is cyclohexyl) in methyl methacrylate (MMA) polymerization.

Results and Discussion

For the above-mentioned reasons, we synthesized guanidinate borohydride derivatives of lanthanides by the reactions of tris(borohydrides) $Ln(BH_4)_3(THF)_n$ with sodium or lithium guanidinates.

We studied the reaction of gadolinium tris(borohydride) $Gd(BH_4)_3(THF)_2$ with two equivalents of $\{(Me_3Si)_2NC(NCy)_2\}Na$, which was prepared *in situ* from $(Me_3Si)_2NNa$ and *N*,*N*-dicyclohexylcarbodiimide, in tetrahydrofuran (65 °C). The separation of the precipitate of $NaBH_4$ that formed, the removal of the solvent *in vacuo*, the treatment of the residue with 1,2-dimethoxyethane (DME), and the subsequent recrystallization of the reaction product from toluene were found to afford the monoguanidinate bis(borohydride) complex $\{(Me_3Si)_2NC(NCy)_2\}Gd(BH_4)_2DME$ (**1**) instead of the bis(guanidinate) borohydride derivative. Complex **1** was isolated in 38% yield (Scheme 1).

Scheme 1



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Transparent colorless crystals of complex **1** were grown by slow evaporation of its toluene solution at room temperature. Complex **1** crystallizes in the space group $P\bar{1}$ with two molecules in the unit cell. The molecular structure of complex **1** is shown in Fig. 1. The selected bond lengths and bond angles are given in Table 1.

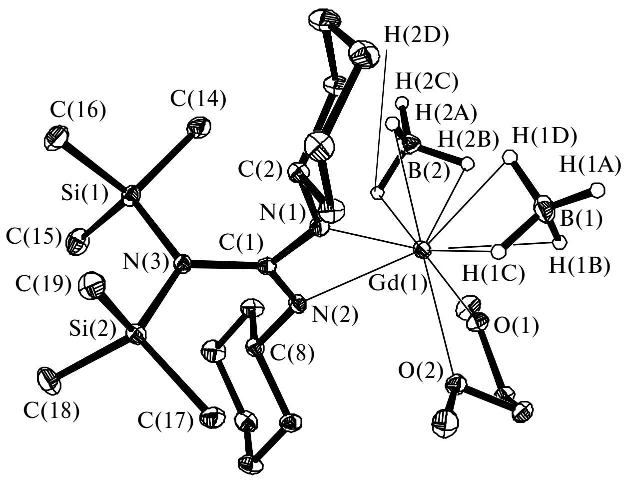


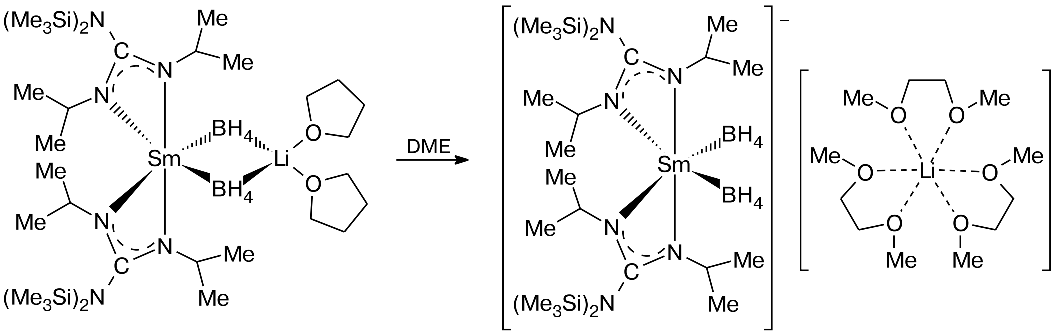
Fig. 1. Structure of the monoguanidinate bis(borohydride) complex $\{(Me_3Si)_2NC(NCy)_2\}Gd(BH_4)_2DME$ (**1**). Displacement ellipsoids are drawn at the 30% probability level.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **1**

Parameter	Value	Parameter	Value
Bond	*d*/Å	Bond	*d*/Å
Gd(1)—N(1)	2.3676(15)	C(1)—N(1)	1.335(2)
Gd(1)—N(2)	2.3797(15)	C(1)—N(2)	1.324(2)
Gd(1)—O(1)	2.4894(13)		
Gd(1)—O(2)	2.4392(14)	Angle	ω/deg
Gd(1)—B(1)	2.596(2)	N(1)—Gd(1)—N(2)	56.09(5)
Gd(1)—B(2)	2.578(2)	B(2)—Gd(1)—B(1)	104.79(9)

The X-ray diffraction study showed that complex **1** exists as a monomer in the crystalline state. The gadolinium atom in compound **1** is coordinated by two nitrogen atoms of the chelate guanidinate ligand, two oxygen atoms of the DME molecule, and two borohydride groups BH_4. The borohydride ligands are μ_3-coordinated to the metal atom through three hydrogen atoms. The Gd—μ_2(H) distances are in the range of 2.27(3)—2.42(3) Å. The Gd—B distances are slightly different (2.578(2) and 2.596(2) Å). The tridentate coordination of the borohydride ligands is confirmed by the IR spectrum of compound **1**, in which these ligands are observed as four broad bands at 2165, 2227, 2338, and 2438 cm^{-1} (see Ref. 10). The Gd—N bond lengths are only slightly different (2.368(2) and 2.380(2) Å). The C—N distances are 1.335(2) and 1.324(2) Å and characterize the negative charge delocalization in the NCN fragment of the guanidinate ligand. The B(1)—Gd—B(2) bond angle in **1** is 104.79(9)°. The Gd—O bond lengths are 2.439(1) and 2.489(1) Å. Only two structurally characterized lanthanide bis(borohydride) complexes, $(C_5Pr^i{}_4H)Nd(BH_4)_2THF$ (see Ref. 14) and $\{(Me_3Si)_2NC(NPr^i)_2\}Sm(BH_4)_2DME$,[18] were described in the literature. When developing procedures for the synthesis of lanthanide bis(guanidinate) borohydride com-

Scheme 2



2

plexes, it was noted[18] that the treatment of the products, which were obtained in the reaction of $Ln(BH_4)_3(THF)_2$ with $(Me_3Si)_2NC(NR_2)M$ (R = Pr^i or Cy; M = Li or Na) in a molar ratio of 1 : 2, with 1,2-dimethoxyethane afforded monoguanidinate bis(borohydride) derivatives. We hypothesized that the ligand redistribution occurs during the treatment of the complexes with dimethoxyethane and is provoked by the replacement of monodentate THF in the coordination sphere of the lanthanide atom by bidentate DME. To verify this hypothesis, we carried out the following experiment. The heterobimetallic complex $\{(Me_3Si)_2NC(NPr^i)_2\}_2Sm(BH_4)_2Li(THF)_2$, whose structure has been determined in our earlier study,[19] was dissolved in DME, and the residue, which was obtained after evaporation of the solution *in vacuo*, was recrystallized from hexane. The recrystallization afforded the $[\{(Me_3Si)_2NC(NPr^i)_2\}_2Sm(BH_4)_2]^-[Li(DME)_3]^+$ complex (**2**) in 63% yield (Scheme 2).

Transparent yellow crystals of complex **2** suitable for X-ray diffraction were grown by slow evaporation of a hexane solution of the complex at room temperature. Complex **2** crystallizes in the space group $P\bar{1}$ with eight molecules in the unit cell. Since the geometric characteristics of independent molecules **2** have similar values, the geometry of only one molecule is discussed below. According to the X-ray diffraction study, compound **2** exists in the crystalline state as a separated ion pair (Fig. 2). Complex **2** consists of the complex anion $[\{(Me_3Si)_2NC(NPr^i)_2\}_2Sm(BH_4)_2]^-$, in which the trivalent samarium cation is coordinated by two guanidinate and two borohydride anions, and the $[Li(DME)_3]^+$ cation. The borohydride ligands are coordinated to the metal atom through the μ_2-bridging hydrogen atoms. The Sm—μ_2(H) distances are in the range of 2.32(4)—2.52(3) Å. The μ_3-coordination of the BH_4 groups is confirmed by the IR spectrum, in which the BH_4 groups are observed as four broad bands at 2235, 2265, 2324, and 2388 cm^{-1}.[7] The Sm—B distances (2.666(5) and 2.680(5) Å; Table 2) are substantially longer than those in the neutral bis(borohydride) complex $\{(Me_3Si)_2NC(NPr^i)_2\}Sm(BH_4)_2DME$ (2.607(3) and 2.615(4) Å)[18] but are substantially shorter than those in the dinuclear complex $[(1,3\text{-}Bu^t{}_2\text{-}C_5H_3)_2Sm(BH_4)]_2$ with the bridging borohydride ligands (2.833(6) and 2.882(6) Å).[20] The Sm—N distances are in the range of 2.436(3)—2.474(3) Å. The C—N bond lengths in the NCN fragments in complex **2** (1.311(4)—1.329(5) Å), like those in complex **1**, are indicative of the electron density delocalization in these fragments. The B(1)—Sm—B(2) bond angle in **2** (94.1(2)°) differs substantially from the corre-

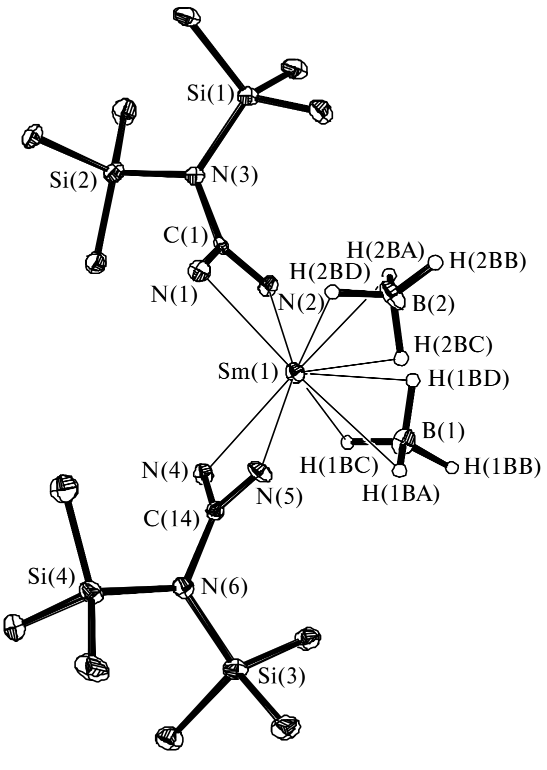


Fig. 2. Structure of the mononuclear ionic complex $[\{(Me_3Si)_2NC(NPr^i)_2\}_2Sm(BH_4)_2]^-[Li(DME)_3]^+$ (**2**). Displacement ellipsoids are drawn at the 30% probability level. The isopropyl substituents at the nitrogen atoms and the $[Li(DME)_3]^+$ cation are omitted.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complex **2***

Parameter	Value	Parameter	Value
Bond	*d*/Å	Bond	*d*/Å
Sm(1)—N(1)	2.467(3)	N(5)—C(14)	1.326(4)
Sm(1)—N(2)	2.474(3)	Sm(1)—B(2)	2.680(5)
Sm(1)—N(4)	2.444(3)		
Sm(1)—N(5)	2.436(3)	Angle	ω/deg
Sm(1)—B(1)	2.666(5)	N(1)—Sm(1)—N(2)	53.86(9)
N(1)—C(1)	1.329(5)	N(5)—Sm(1)—N(4)	54.38(9)
N(2)—C(1)	1.311(4)	B(1)—Sm(1)—B(2)	94.1(2)
N(4)—C(14)	1.323(4)		

* The geometric characteristics for one independent molecule are given.

sponding angle in the neutral bis(borohydride) complex $\{(Me_3Si)_2NC(NPr^i)_2\}Sm(BH_4)_2DME$ (102.52(13)°).[18] It was of interest to consider the differences in the geometry of mononuclear complexes **2** and $\{(Me_3Si)_2NC(NPr^i)_2\}Sm(BH_4)_2DME$ in terms of the filling of the coordination sphere of Sm cations. The calculated degree of filling of the coordination sphere of samarium in **2** is 85.5(2)%,[21] which is substantially larger than that in $\{(Me_3Si)_2NC(NPr^i)_2\}Sm(BH_4)_2DME$ (81.6(2)%), and, consequently, the nonbonded interactions between the ligands in the coordination sphere of **2** should also be somewhat stronger. Apparently, due to this fact the Sm—B and Sm—N distances in **2** (2.436(3)—2.474(3) Å) are longer than those in $\{(Me_3Si)_2NC(NPr^i)_2\}Sm(BH_4)_2DME$ (Sm—N, 2.374(2)—2.395(2) Å), whereas the BSmB angle is smaller. In addition, it becomes clear why the treatment of the heterobimetallic complex $\{(Me_3Si)_2NC(NPr^i)_2\}_2Sm(BH_4)_2Li(THF)_2$ with dimethoxyethane affords the separated ion pair (**2**). The Li cation is shielded by three DME molecules, and the degree of filling of its coordination sphere is 89.7(7)%. Apparently, this is the reason why this cation cannot be coordinated by BH_4^- anions.

Therefore, it can be concluded that the treatment with dimethoxyethane can lead to the transformation of the heterobimetallic complexes $\{(Me_3Si)_2NC(NPr^i)_2\}_2Sm(BH_4)_2Li(THF)_2$ into the ionic complexes $[\{(Me_3Si)_2NC(NPr^i)_2\}_2Sm(BH_4)_2]^-[Li(DME)_3]^+$; however, no disproportionaion of the complexes was observed.

Compounds **1** and **2** are sensitive to atmospheric oxygen and moisture, but they are stable during storage over a long period of time *in vacuo* or under an inert atmosphere at room temperature. Complexes **1** and **2** are readily soluble in ethers, as well as in aromatic and even aliphatic hydrocarbons, which substantially hinders their isolation by recrystallization and decreases the yields of the crystalline products.

It is known that lanthanide borohydride complexes are catalytically active in the polymerization of both polar (methyl methacrylate[22] and ε-caprolactone[11]) and nonpolar (isoprene)[14] monomers. As expected, the catalytic properties of metallocene-type borohydride derivatives have been studied in most detail, whereas the data on the catalytic properties of borohydride complexes in the noncyclopentadienyl ligand environment are still scarce.

Recently,[15] we have reported the synthesis and structures of the $\{(Me_3Si)_2NC(NCy)_2\}_2Ln(BH_4)_2Li(THF)_2$ complexes (Ln = Nd (**3**), Sm (**4**), or Yb(**5**)), which proved to be active catalysts for the polymerization of lactides accompanied by the ring opening. The use of complexes **3**—**5** as initiators for the polymerization of lactides allows the reaction to be performed at high rate at room temperature under controlled conditions resulting in the formation of high-molecular-weight polymers with very low polydispersity (1.09).[15] Hence, it was of interest to study the catalytic activity of the resulting complexes in the polymerization of other polar monomers, for example, of MMA. We investigated the catalytic activity of complexes **3**—**5** in MMA polymerization. The reaction was carried out in toluene at (21±0.5) °C under conditions precluding exposure to atmospheric oxygen and moisture with the use of different catalyst-to-monomer ratios. The rate of polymerization in the initial step (up to the conversion of 10%) was measured by the dilatometric method, and the weighting method was used for studying higher degrees of conversion. Since the polymerization catalyzed by samarium complex **4** starts already at negative temperatures, the rate of polymerization at 21 °C cannot be studied by the dilatometric method.

Figures 3 and 4 show the plots of the degree of conversion of MMA *vs.* the reaction time at different concentrations of complexes **3** and **5**. It can be seen that the time dependence of the conversion has a linear character at lower degrees of conversion.

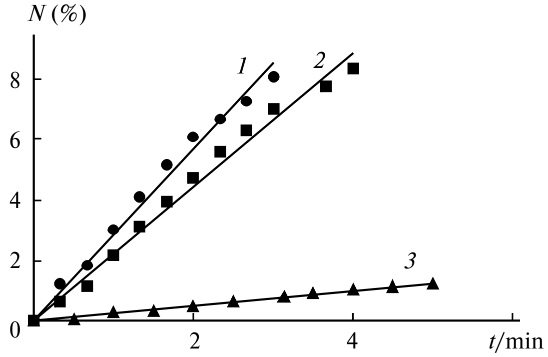


Fig. 3. Plot of the conversion (*N*) of methyl methacrylate *vs.* the time of polymerization in the presence of complex **3** (T = 21±0.5 °C; toluene; C_0^{Cat}/mol L^{-1}: 5.70 • 10^{-3} (*1*), 4.66 • 10^{-3} (*2*), 3.00 • 10^{-3} (*3*); C_0^{MMA}/mol L^{-1}: 4.67 (*1*), 4.66 (*2*), 4.65 (*3*), C_0^{MMA}/C_0^{cat}: 1/820 (*1*), 1/1000 (*2*), 1/1550 (*3*)).

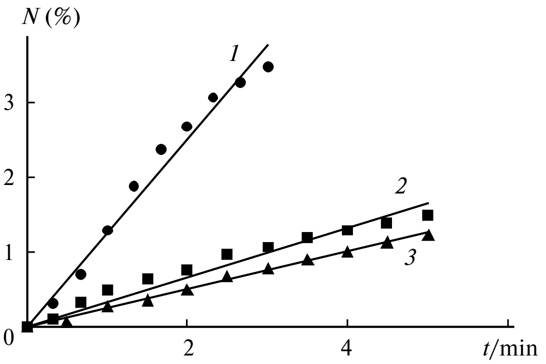


Fig. 4. Plot of the conversion (N) of methyl methacrylate *vs.* the time of polymerization in the presence of complex **5** (T = 21±0.5 °C; toluene; $C_0^{\rm Cat}$/mol L^{-1}: 5.70$\cdot$10^{-3} (*1*), 4.66$\cdot$10^{-3} (*2*), 3.00$\cdot$10^{-3} (*3*); $C_0^{\rm MMA}$: 4.65/mol L^{-1} (*1—3*); $C_0^{\rm MMA}/C_0^{\rm cat}$: 1/816 (*1*), 1/1000 (*2*), 1/1550 (*3*)).

A comparison of the catalytic activities of complexes **3** and **5** at the catalyst-to-monomer ratios under study shows that neodymium complex **3** is more active in MMA polymerization. For example, the conversion with the use of complex **3** as the catalyst ($[\mathrm{MMA}]_0/[\mathbf{3}]_0$ = 1/820) reaches 8% during 3 min, whereas the conversion in the presence of ytterbium complex **5** during this time is lower than 4%. The investigation of the catalytic activity of complexes **3**—**5** in MMA polymerization at higher degrees of conversion was performed by the weighting method (T = 21±0.5 °C; $C_0^{\rm Cat}$ = 0.3$\cdot$10^{-2} mol L^{-1}; $[\mathrm{MMA}]_0/[\mathrm{Cat}]_0$ = 1/1550). The catalytic activity of the lanthanide bis(guanidinate) borohydride complexes in the methyl methacrylate polymerization decreases in the series Sm > Nd > Yb (Fig. 5). Therefore, no correlation between the catalytic activity of complexes **3**—**5** in MMA polymerization and the ionic radius of lanthanides was observed (ionic radii: Nd, 0.983 Å; Sm, 0.958 Å; Yb, 0.868 Å).[23]

In the methyl methacrylate polymerization in the presence of samarium complex **4**, the conversion reaches 62.3% during 8 h. The reaction affords a polymer with the molecular weight $M_{\rm w}$ = 88856 g mol^{-1}, $M_{\rm n}$ = 57979 g mol^{-1} and the polydispersity factor $M_{\rm w}/M_{\rm n}$ = 1.53. According to the NMR data, the polymerization affords a heterotactic polymer, with syndiotactic triads predominating. The percentage of iso-, hetero-, and syndiotactic triads is 51, 12, and 37%, respectively. The reaction rate of polymerization in the presence of neodymium complex **4** is substantially lower. The conversion reaches 39.4% during the same time. The resulting polymer has the higher molecular weight ($M_{\rm w}$ = 226139 g mol^{-1}, $M_{\rm n}$ = 615045 g mol^{-1}) and a broader molecular weight distribution ($M_{\rm w}/M_{\rm n}$ = 2.72). In the heterotactic polymer, the percentage of iso-, hetero-, and syndiotactic triads is 31, 34, and 35%, respectively. Ytterbium complex **5** is the least active in the series of the compounds under consideration; the yield of PMMA is 32.1% after 8 h. The resulting polymerization has the molecular weight $M_{\rm w}$ = 94130 g mol^{-1}, $M_{\rm n}$ = 57726 g mol^{-1}, and the polydispersity factor $M_{\rm w}/M_{\rm n}$ = 1.63. In the resulting heterotactic polymer, the percentage of iso-, hetero-, and syndiotactic triads is 52, 32, and 16%, respectively. For all three catalysts, the kinetic curves flatten within 6—7 h (see Fig. 5), and the yield of the polymer changes only slightly with reaction time. Most likely, this observation is attributed to the decomposition of the catalyst in the course of polymerization.

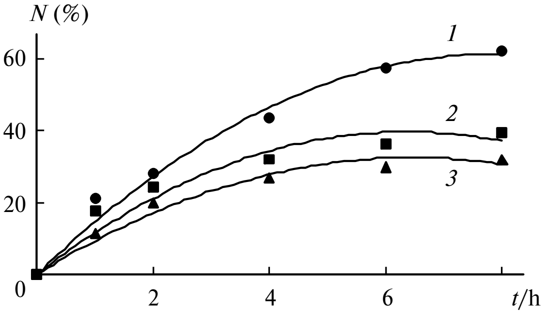


Fig. 5. Plot of the conversion of MMA *vs.* the time of polymerization in the presence of complexes **3** (*1*), **4** (*2*), and **5** (*3*) ($C_0^{\rm Cat}$ = 3.00$\cdot$10^{-3} mol L^{-1}; $C_0^{\rm MMA}$ = 4.65 mol L^{-1}; $C_0^{\rm MMA}/C_0^{\rm cat}$ = 1/1550, toluene, T = 21±0.5 °C).

To summarize, we synthesized the new guanidinate bis(borohydride) complex $[(\mathrm{Me_3Si})_2\mathrm{NC(NCy)_2}]\mathrm{Gd(BH_4)_2DME}$ (**1**). The treatment of the heterobimetallic complex $\{(\mathrm{Me_3Si})_2\mathrm{NC(NPr^i)_2}\}_2\mathrm{Sm(BH_4)_2Li(THF)_2}$, which contains two bridging borohydride anions between the samarium and lithium atoms, with dimethoxyethane affords the ionic complex $[\{(\mathrm{Me_3Si})_2\mathrm{NC(NPr^i)_2}\}_2\mathrm{Sm(BH_4)_2}]^-[\mathrm{Li(DME)_3}]^+$ (**2**). However, no disproportionation of the complexes was observed. The $\{(\mathrm{Me_3Si})_2\mathrm{NC(NCy)_2}\}_2\mathrm{Ln(BH_4)_2Li(THF)_2}$ complexes (Ln = Nd (**3**), Sm (**4**), or Yb (**5**)) catalyze MMA polymerization at room temperature, the catalytic activity of the complexes decreasing in the series Sm > Nd > Yb.

Experimental

The complexes were synthesized under conditions precluding exposure to atmospheric oxygen and moisture with the use of the standard Schlenk technique. Tetrahydrofuran, hexane, and toluene were dried over sodium benzophenone ketyl, thoroughly degassed, and condensed *in vacuo* into a reaction tube immediately before use. The IR spectra were recorded on a Specord M80 instrument as degassed Nujol mulls. The ^{1}H, ^{7}Li, ^{11}B, and ^{13}C NMR spectra were measured on a Bruker DPX 200 instrument. Anhydrous $\mathrm{LnCl_3}$,[24] $(\mathrm{Me_3Si})_2\mathrm{NLi(Et_2O)}$, and $(\mathrm{Me_3Si})_2\mathrm{NNa}$,[25] as well as $\mathrm{Ln(BH_4)_3(THF)}_n$,[26] were synthesized according to known procedures. N,N'-Diisopropylcarbodiimide, N,N'-dicyclohexylcarbodiimide, and $\mathrm{NaBH_4}$ were commercial reagents (Acros). *N*,*N*′-Diisopropylcarbodiimide was used after drying with A4 molecular sieves and condensation *in vacuo*; NaBH$_4$ was used without additional purification. The chemical shifts are given in ppm relative to the known shifts of the residual protons of the deuterated solvents. The molecular weight distribution was determined on a Waters gel permeation chromatograph equipped with a R-403 differential refractometer (Waters) as the detector with the use of tetrahydrofuran as the eluent. The calibration was performed with narrow-disperse polystyrene standards.

[*N*,*N*′-Dicyclohexyl-*N*′-bis(trimethylsilyl)guanidinate]-bis(borohydride)gadolinium(III) dimethoxyethanate, {(Me$_3$Si)$_2$NC(N-Cy)$_2$}Gd(μ^{3-}BH$_4$)$_2$DME (1). The Gd(BH$_4$)$_3$(THF)$_2$ compound (0.73 g, 2.11 mmol) was added to a solution of sodium guanidinate, which was prepared by the reaction of (Me$_3$Si)$_2$NNa (0.76 g, 4.15 mmol) with *N*,*N*′-dicyclohexylcarbodiimide (0.86 g, 4.17 mmol), in THF (50 mL). The reaction mixture was stirred at 65 °C for 14 h. Tetrahydrofuran was removed by vacuum condensation, and the solid residue was extracted with toluene to separate NaBH$_4$ that formed. The toluene extract was filtered, and toluene was removed *in vacuo* at room temperature. The solid residue was dissolved in DME (15 mL), and the solvent was removed *in vacuo* at room temperature. After recrystallization of the residue from toluene, colorless crystals of **1** were obtained in a yield of 0.25 g (0.39 mmol, 38%). Found (%): C, 42.35; H, 9.33; Gd, 24.17. $C_{23}H_{58}B_2GdN_3O_2Si_2$. Calculated (%): C, 42.91; H, 9.08; Gd, 24.43. IR (Nujol mulls), ν/cm^{-1}: 2438, 2338, 2227, 2165, 1638, 1304, 1254, 1180, 1050, 1008, 942, 865, 842, 757, 723, 680, 642.

Bis[*N*,*N*′-diisopropyl-*N*′′-bis(trimethylsilyl)guanidinate]-di(tetrahydroborato)tris(dimethoxyethane)lithiumsamarium(III), [{(Me$_3$Si)$_2$NC(N-Pr^i)$_2$}$_2$Sm(BH$_4$)$_2$]$^-$[Li(DME)$_3$]$^+$ (2). The {(Me$_3$Si)$_2$NC(N-Pr^i)$_2$}$_2$Sm(BH$_4$)$_2$Li(THF)$_2$ complex (0.17 g, 0.19 mmol) was dissolved in DME. Then DME was removed *in vacuo* at room temperature. The solid residue was dissolved in hexane (20 mL). The hexane solution was slowly concentrated at room temperature, and yellow crystals of complex **2** were obtained in a yield of 0.124 g (0.12 mmol, 63%). Found (%): C, 43.82; H, 10.15; Sm, 14.22. $C_{38}H_{102}B_2LiN_6O_6Si_4Sm$. Calculated (%): C, 44.29; H, 9.98; Sm, 14.59. IR (Nujol mulls), ν/cm^{-1}: 2388, 2324, 2265, 2235, 1638, 1327, 1257, 1116, 1081, 1049, 956, 920, 842, 760, 686, 662.

Methyl methacrylate polymerization catalyzed by complexes 3, 4, and 5 (general procedure). Methyl methacrylate (1.81 g, 18.1 mmol) was added to a solution of complex **3** (0.0128 g, 0.012 mmol) in toluene (1.94 mL), and the mixture was placed in a thermostat at 21±0.5 °C. After 8 h, the reaction tube was opened, air was admitted into the tube, and one drop of methanol was added. The solution was filtered to separate the hydrolysis products of the catalyst. Then the polymer was precipitated from the toluene solution with hexane, filtered off, washed with methanol and hexane, and dried to constant weight *in vacuo* at room temperature. Poly(methyl methacrylate) was isolated in a yield of 1.13 g.

X-ray diffraction study. Experimental X-ray intensities were measured on an automated Smart APEX diffractometer (graphite monochromator, MoKα radiation, ω—φ-scanning technique) at 100 K. All structures were solved by direct methods and refined by the least-squares method based on F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms. All H atoms (except for the hydrogen atoms of the BH$_4$ groups) were positioned geometrically and refined using a riding model. The hydrogen atoms of the BH$_4$ groups were located in differ-

Table 3. Crystallographic parameters and the X-ray diffraction data collection and refinement statistics for complexes **1** and **2**

Parameter	1	2
Molecular formula	$C_{23}H_{58}B_2GdN_3O_2Si_2$	$C_{38}H_{102}B_2LiN_6O_6Si_4Sm$
Molecular weight	643.77	1030.52
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	8.3942(5)	23.3000(8)
b/Å	10.3568(6)	23.6675(8)
c/Å	19.740 (1)	24.1504(8)
α/deg	98.293(1)	98.184(1)
β/deg	97.319(1)	97.248(1)
γ/deg	101.776(1)	112.722(1)
V/A^3	1640.6(2)	11917.4(7)
Z	2	8
ρ_{calc}/g cm^{-3}	1.303	1.149
μ/mm^{-1}	2.116	1.106
θ-Scan range/deg	2.04 – 29.18	1.61 – 25.00
Number of measured reflections	17095	94273
Number of reflections with $I > 2\sigma$	8561 (R_{int} = 0.0157)	41805 (R_{int} = 0.0764)
Number of variables	330	2268
Goodness-of-fit	1.084	0.922
R_1/wR_2 ($I > 2\sigma(I)$)	0.0219/0.0552	0.0513/0.0950
R_1/wR_2 (based on all reflections)	0.0236/0.0563	0.1061/0.1070
Residual electron density, max/min, e Å^{-3}	1.153/–0.765	1.537/–0.616

ence electron density maps and refined isotropically. All calculations were carried out with the use of the SHELXTL v. 6.10 program package.[27] Absorption corrections were applied using the SADABS program.[28] Principal crystallographic parameters and the X-ray diffraction data collection and refinement statistics are given in Table 3. The atomic coordinates were deposited with the Cambridge Structural Database (CCDC 649132 and 649133 for complexes **1** and **2**, respectively). The spectroscopic and X-ray diffraction studies were carried out at the Analytical Center of the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences.

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